A Contribution to the Theory of Polarization of Porous Electrodes

Karel Micka

Polarographic Institute, Czechoslovak Academy of Science,   Prague

Introduction

The problem of polarization of porous electrodes with relation to the resistance of the electrode material was solved first by Coleman (1) in the case of cylindrical cathodes of Leclanché elements. In his differential equation, a supposition is implicitly included that the faradayic current, u, is directly proportional to the polarization of manganese dioxide particles, although he considered the "electromotive force of the manganese dioxide particle" as constant. Therefore, Coleman's expression for the faradayic current as a function of the distance from electrode surface is substantially in accord with that of Euler and Nonnenmacher (2) who assumed a linear polarization curve of manganese dioxide electrode. Daniel-Bek (3) was the first to deduce fundamental differential equations in the form which is used nowadays. He gave the solution for two limiting cases, viz., that the faradayic current is an exponential or a linear function of polarization. Finally, Newman and Tobias (4) solved the differential equations under the supposition that the faradayic current is an exponential function of polarization and their results are substantially in accord with those of Daniel-Bek.

None of the mentioned authors' solutions is valid for the whole polarization region, but only for limiting cases of either small or large overvoltage. However, it is possible to deduce a generally valid solution, as follows.

Mathematical solution

For exactness, let us consider an electrode of rectangular shape with pores in form of linear channels parallel to one edge of the electrode, although it is possible to abandon any assumption concerning

the geometry of the pores (4). The x-axis runs parallel to the pores, on the electrolyte side being x = 0. A metallic conductor as current collector is placed on the end of the pores, at x = L. For potential, φ_1, in the electrode material, Ohm's law holds:

$$\frac{d\varphi_1}{dx} = -\rho_1 i_1 , \qquad\qquad /1/$$

where ρ_1 is the resistance of a cubic centimeter of the porous electrode material in the direction of x-axis, and i_1 is the electronic current density corresponding to 1 sq. cm. of the electrode section perpendicular to the x-axis.

When the electrode consists of a depolarizer and an excess supporting electrolyte, and when the concentration polarization can be neglected with respect to the activation and resistance polarization, then an analogous equation holds for the potential, φ_2, in the electrolyte:

$$\frac{d\varphi_2}{dx} = -\rho_2 i_2 , \qquad\qquad /2/$$

where ρ_2 is the resistance of the electrolyte contained in one cubic centimeter of the electrode, and i_2 is the ionic current density corresponding again to 1 sq. cm. of the electrode section. Finally, according to Daniel-Bek (3), we may write the following equation for the density of faradayic current, D, on the inner pore surface:

$$\frac{d i_2}{dx} = -SD , \qquad\qquad /3/$$

where S is the inner surface of a cubic centimeter of the electrode. Let us choose for D the following function of polarization /overvoltage/, E:

$$D = 2i_o \sinh \beta E, \qquad\qquad /4/$$

where $E = \varphi_2 - \varphi_1$ fulfills the condition that E = 0 when D = 0, i_o is the exchange current density, and $\beta = F/2RT$; it is possible, however, to substitute for β an empirical value obtained by measurement of polarization curves with a planar electrode. For anodic and cathodic polarization, the values of β can be different. Therefore, it would be more correct to use the well known general relation between current and overvoltage from the theory of absolute reaction rates, rather than equation /4/. In that case, however, the mathematical solution would become too complicated, without yielding any substantial improvement.

The boundary conditions for equations /1/-/3/ are:

$$x = 0: \quad i_1 = 0, \quad \varphi_2 = 0, \qquad\qquad /5/$$

$$x = L: \quad i_1 = I, \tag{/6/}$$

and the conservation law of current:

$$i_1 + i_2 = I. \tag{/7/}$$

For a cathodic current, $I > 0$, $E > 0$, and $D > 0$; for an anodic current, $I < 0$, $E < 0$, and $D < 0$. The problem defined by equations /1/-/7/ can be reduced to the following differential equation:

$$\lambda^2 \frac{d^2 u}{dx^2} = \sinh u \tag{/8/}$$

with boundary conditions:

$$x = 0: \quad \frac{du}{dx} = -\beta \rho_2 I, \tag{/9/}$$

$$x = L: \quad \frac{du}{dx} = \beta \rho_1 I, \tag{/10/}$$

with $u = \beta E$, and $\lambda = 1/\sqrt{2i_0 S \beta (\rho_1 + \rho_2)}$.

The solution of equations /8/-/10/ is:

$$|x - x_m| = k\lambda F(k, \psi), \tag{/11/}$$

where $F(k, \psi)$ stands for the elliptic integral of the first kind with the modulus

$$k = \frac{1}{\cosh \frac{1}{2} u_m}, \tag{/12/}$$

and amplitude

$$\psi = \arccos \frac{\sinh \frac{1}{2} u_m}{\sinh \frac{1}{2} u}. \tag{/13/}$$

Further x_m is the value of x at which $|u|$ has the minimum value $|u_m|$. Formally, the solution /11/ is analogous to that which Winsel (5) derived for the case of $\rho_1 = 0$.

The expression for faradayic current takes the form:

$$D = \frac{D_m}{\cos^2 \psi} \sqrt{1 - k^2 \sin^2 \psi} \tag{/14/}$$

ψ being defined by equation /11/ as

$$\sin \psi = sn \left(\frac{|x - x_m|}{k\lambda}, k \right), \tag{/15/}$$

where sn denotes Jacobi's elliptic function. Further D_m stands for $2i_0 \sinh u_m$, so that $|D_m|$ represents the minimum value of $|D|$.

An important measurable quantity is the potential, φ_{1L}, of the metallic conductor at the end of the pores /vs. the electrolyte potential at $x = 0$/. For this we obtain:

$$\varphi_{1L} = - \frac{\rho_2}{\rho_1 + \rho_2}(E_0 + IL\rho_1) - \frac{\rho_1}{\rho_1 + \rho_2}E_L , \qquad /16/$$

where E_0 and E_L are the values of E for $x = 0$ and $x = L$, which fulfill the following relationship:

$$\cosh \beta E_0 - \cosh \beta E_L = \frac{1}{2}\beta^2 \lambda^2 I^2 (\rho_2^2 - \rho_1^2). \qquad /17/$$

The value of E_0 can be computed from the equation

$$\sinh \frac{1}{2}\beta E_0 = \frac{I}{I_0 \sin \gamma_0} , \qquad /18/$$

where $I_0 = 2/\beta\lambda\rho_2$, and γ_0 is the solution of the equation

$$\frac{L}{k\lambda} = F(k, \gamma_0) + F(k, \gamma_L) \qquad /19/$$

with $\gamma_L = \text{arctg}\left[(\rho_1/\rho_2)\,\text{tg}\,\gamma_0\right]$, and $k = 1/\sqrt{1 + I^2/I_0^2 \text{tg}^2 \gamma_0}$.

Some limiting cases

When the pores are short so that $L < \frac{1}{2}\pi k\lambda$ and the current is large, then $k \ll 1$ and the expression for faradayic current becomes:

$$D = D_m \sec^2 \frac{x - x_m}{k\lambda} . \qquad /20/$$

In this case, the polarization of the electrode is large, so that the hyperbolic sine in equation /4/ may be substituted by an exponential function. Equation /20/ can be shown to correspond exactly to the solution given by Newman and Tobias (4).

When, on the contrary, the pores are long and the current small, so that $|I| \ll I_0 \sinh(L/2\lambda)$, equation /14/ becomes

$$D = D_m \cosh \frac{x - x_m}{\lambda} \sqrt{k^2 + (1-k^2)\cosh^2 \frac{x-x_m}{\lambda}} . \qquad /21/$$

When, in addition, the polarization of the electrode is small, so that the hyperbolic sine in equation /4/ may be substituted by a linear function, we can set $k = 1$ in equation /21/ to obtain a simple formula which /after suitable rearrangement/ can be shown to correspond exactly to the solution given by Euler and Nonnenmacher (2).

When the specific resistances of both phases, electrode and electrolyte, are equal, then equation /17/ yields simply $E_0 = E_L$, so that the polarization at one end of the pores is equal to that at the other.

Further $x_m = \frac{1}{2} L$, that is, the minimum of the absolute value of polarization is in the middle of the electrode. Hence, the faradayic current distribution in the electrode is symmetrical. Equation /16/ becomes

$$\varphi_{1L} = -E_o - \frac{1}{2} IL\rho_1 . \qquad\qquad /22/$$

When the specific resistance of the electrode is negligible, so that $\rho_1/\rho_L \rightarrow 0$, we have the case allready discussed by Winsel (5); then $\varphi_{1L} = -E_o$, $x_m = L$. On the contrary, when the specific resistance of the electrode is very great, so that $\rho_1/\rho_L \rightarrow \infty$, we have $\varphi_{1L} = -E_L$, $x_m = 0$. The results of Winsel (5) can be applied in this case, if we introduce a new independent variable $x' = L - x$. In other words, we consider the end of the pores as the beginning and vice versa.

An interesting and very simple case is when the specific resistances of both phases are equal and, simultaneously, the pores are long and/or the current is small. Then we can express φ_{1L} simply as a function of the current, I:

$$\varphi_{1L} = - \frac{2}{\beta} \operatorname{arsinh} \left(\frac{I}{I_o} \coth \frac{L}{2\lambda} \right) - \frac{1}{2} IL\rho_1 , \qquad\qquad /23/$$

from which it can be seen that the electrode polarization, φ_{1L}, is directly proportional to the total current when $|I| \ll I_o$. Further, we can define the initial polarization resistance as

$$R = -\left(\frac{\partial \varphi_{1L}}{\partial I}\right)_{I=0} = \frac{2}{I_o\beta} \coth \frac{L}{2\lambda} + \frac{1}{2} L\rho_1 . \qquad\qquad /24/$$

The symmetrical form of faradayic current distribution can be readily seen from equation /21/, if we set $x_m = L/2$.

Other cases are more complicated and we have to compute the polarization curves, $\varphi_{1L} = f(I)$, numerically for a given set of parameters I_o, L, λ, ρ_1 and ρ_L. This will be the purpose of further work.

References

1. J.J. Coleman: Trans. Electrochem. Soc. 90, 545 /1946/.
2. J. Euler and W. Nonnenmacher: Electrochim. Acta 2, 268 /1960/.
3. V.S. Daniel-Bek: Zhur. Fiz. Khim. 22, 697 /1948/.
4. J.S. Newman, Ch.W. Tobias: J. Electrochem.Soc.109,1183/1962/.
5. A. Winsel: Z. Elektrochem. 66, 287 /1962/.